



Electrocatalytic reduction of chromium by poly(aniline-co-o-aminophenol): An efficient and recyclable way to remove Cr(VI) in wastewater

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ABSTRACT

Poly(aniline-co-o-aminophenol) (PANOA)-modified glassy carbon electrode (GCE) was first used to investigate the electrocatalytic reduction of dichromate in a NaCl solution of pH 5.0. The results of cyclic voltammograms and UV-vis spectra demonstrated that the reduction of Cr(VI) occurred at PANOA-modified GCE. The FT-IR, ESR and XPS results showed that the Cr(VI) can be doped in the PANOA films and can convert to less-toxic Cr(III). The doping level Cr/N was 78.2% and trace amount of Cl (0.42%) was detected in the doped PANOA, which indicated that the doping process is effective and PANOA had rather good ion selectivity in the 0.10 M NaCl supporting electrolyte. The factors influenced the reduction were also considered. Various initial concentrations of Cr(VI) had different removal rates. The maximum removal rate of Cr(VI) at 20 mg L⁻¹ (32.3%) was better than that of at 5 mg L⁻¹ (22.9%). The solution pH had little effect on Cr(VI) reduction and doping process of the PANOA because PANOA had good electrochemical activity and stability in a wide range of pHs (from pH 4 to pH 8).

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1. Introduction

Chromium is considered as a priority pollutant for its high toxicity to plants and animals. Chromium contamination mainly comes from industrial process, including tannery facilities, pigment production, antibiofoulant in cooling towers and metal planting etc. [1–3]. In aqueous environment, chromium exists in two common oxidation states, Cr(VI) and Cr(III). Hexavalent chromium usually occurs in aqueous phase as oxyanions (HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ or CrO_4^{2-}) [4]. Cr(III) is generally less-toxic or nontoxic to animals, while Cr(VI) is a strong oxidant that acts as carcinogens and mutagens in biological systems [5–6]. Therefore, it is of great urgent to develop new technologies to remediate Cr(VI) contamination.

Many methods have been tried for the removal of Cr(VI) from wastewater, including reverse osmosis, adsorption, and ion exchange [7,8,19–13]. But the most widely used technique for Cr(VI) removal is chemical reduction followed by precipitation [14]. Though the chemical treatment is easy to implement, it needs continual energy and reagents supply. The use of electrochemical approach to removal metal ions in wastewater is considered to be a simple and clean method [15–17]. No additional chemical loading is required for the process, and electricity is the only input [18]. Consequently, the electrochemical process is promising for the treatment of Cr(VI) in wastewater.

Conducting polymers such as polyaniline have been used in many fields including corrosion protection, secondary rechargeable batteries, sensors and controlled drug delivery [19–22]. Recent studies have shown that conducting polymer film can be used to reduce Cr(VI) [23,24]. Yang and Huang have used a polyaniline/polystyrene composite electrode for the detection and analysis of Cr(VI) [25]. All these reports present a new realm of application for conducting polymers in toxic waste treatment. The oxidation of the conducting polymer is accompanied with incorporation of anions of the solution into the conducting polymer, i.e. doping; the reduction of the conducting polymer is accompanied with release of anions from the conducting polymer into the solution, i.e. dedoping. Therefore, the doping and dedoping principle of the conducting polymers forms a new concept for the removal of Cr(VI) from wastewater.

As mentioned above, the conducting polymers (e.g. polyaniline) have been used successfully in the reduction of Cr(VI). However, they are only effective in a limited acidic pH range. A novel conducting copolymer poly(aniline-co-o-aminophenol) (PANOA), synthesized and characterized by Mu and co-workers [26–28], has been shown by voltammetry to be active and stable over a wider pH range (from pH <1 to pH 10) than other conducting polymers. Therefore, it is a promising material for removing Cr(VI) from solutions for its excellent redox activity in a wide range of pHs. Furthermore, the reversibility of the PANOA enables the electrochemical recycling of the PANOA for repeated treatment of Cr(VI).

In this paper, the PANOA-modified glassy carbon electrode was first used to investigate the electrocatalytic reduction and recycle

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of chromium in a wide range of solution pHs (from pH 4 to pH 8). The PANO film was characterized by cyclic voltammetry, UV–vis, FT-IR and ESR spectra, and X-ray photoelectron spectroscopy (XPS). An efficient and recyclable reduction of Cr(VI) was confirmed by XPS. Furthermore, the possible mechanism of electrocatalytic reduction and recycle of chromium was proposed.

2. Experimental

2.1. Materials

Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) and other chemicals were of analytical reagent grade obtained from Shanghai Chemical Company. Aniline was distilled under reduced pressure prior to use. All solutions were prepared with doubly distilled water. An electrolytic cell for the synthesis of the PANO copolymer consisted of a GC working electrode (3 mm diameter, CHI), a home-made 64 mm² platinum foil counter electrode and a saturated calomel reference electrode (SCE) except stated otherwise. All potentials were referred to a SCE. The glassy carbon electrode (GCE) was polished with alumina slurry of 0.5 μm on polishing cloth with water and then thoroughly rinsed with water and sonicated in a doubly distilled water bath for 10 min before use.

2.2. Instruments

Cyclic voltammetry was performed in the electrolytic cell consisted of a GC working electrode (3 mm diameter, CHI), a 64 mm² platinum foil counter electrode and a saturated calomel reference electrode on a Model CHI 407 electrochemical workstation. Chronoamperometry was carried out on a Model MCP-1 potentiostat–galvanostat with a Model LZB-B digital coulometer (Jiangsu Electroanalytical Instrument Company, China). The UV–vis spectra of all samples were obtained with a UV-2450 spectrometer (Shimadzu, Japan) in the range 200–800 nm. The FT-IR spectra of PANO samples were measured on a pressed pellet with KBr using a Bruker IFS 66/s spectrometer. The ESR measurements were carried out using a Bruker A300 spectrometer operated in X-band (9.862 GHz). The modulation amplitude was set to 1.0 G. Bruker Company provided a g -factor marker of $\text{S}^{3/2}$; and its g -value is 1.9800 ± 0.0006 . The spectrum of the X-ray photoelectron spectroscopy of the sample was measured on a Thermo ESCALAB 250 spectrometer with an Al K_{α} X-ray source (1486.6 eV). All binding energies were referred to C_{1s} neutral carbon peak at 284.6 eV. Flame atomic absorption spectroscopy (Solaar, M 6) was used to detect the total Cr. The pH values of the solutions were determined with a PXD-12 meter.

3. Results and discussion

3.1. Preparation and stability of PANO-modified GCE

The PANO films were synthesized at 0.79 V in an electrolytic cell consisting of a glassy carbon working electrode, a platinum foil counter electrode and a saturated calomel reference electrode. The electrolytic solution consisted of 0.3 M aniline, 5.5 mM *o*-aminophenol and 2.0 M HCl. Fig. S1 shows the change in the current with time for the electrolysis of the above solution with stirring. As shown in Fig. S1 that the current first decreases and then increases quickly and finally reaches the steady-state value. The former is caused by the concentration polarization and the formation of the PANO film with lower conductivity than that of GCE. And the latter is caused by autocatalytic copolymerization as well as the electrochemical polymerization of aniline and the growth of its electroactive film. The result shown in Fig. S1 demonstrates that the copolymerization rate is rather fast. The charge consumed in the copolymerization was monitored and controlled to 0.35 C except stated otherwise. After synthesis, the PANO films were washed with 0.05 M HCl solution to remove unreacted reactants, rinsed with doubly distilled water before transferred to 0.10 M NaCl.

Fig. 1A depicts the cyclic voltammograms (CV) of a PANO-modified GCE immersed in 0.10 M NaCl solution with pH 5.0. CVs of the copolymer film reached the stable state after 9–10 cycles. A well-defined oxidation peak was established at 0.28 V, with a broad plateau observed on reverse scans, which means that the electrochemically synthesized PANO film is reversible and stable at pH 5.0. Similar redox property was reported for PANO in Na_2SO_4 solution around pH 10.0 [26,27]. For both cases, the electroactive decay from the first cycle to the ninth cycle could be explained by the pH difference between the bulk solution and that in the inner polymer matrix, which needs time to reach equilibrium. CV for PANO in 0.20 M HCl solution (Fig. S2) was very similar to that of polyaniline in 1.0 M HCl [26], indicating that it also achieves a high redox activity in the acid solution. Hence, the PANO is conductive and reversible in redox processes. The prepared PANO-modified GCE was then transferred to a 4 mL dichromate solution.

3.2. Electrocatalytic reduction and removal of Cr(VI) by PANO-modified GCE

Fig. 1B shows the cyclic voltammograms of PANO in the solution of 0.10 M NaCl without (curve 1) and with various concentrations of dichromate (1–40 mM) (curves 2–4) with pH 5.0. The wave shape of curve 4 of PANO in a solution containing

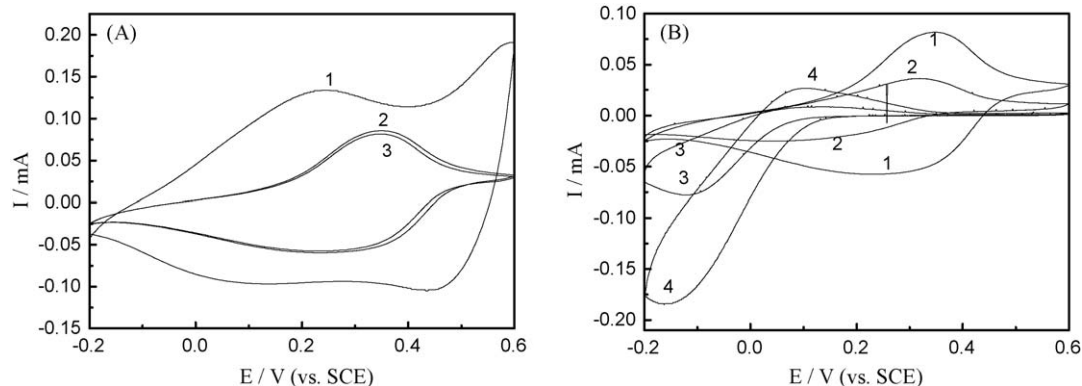


Fig. 1. (A) Cyclic voltammograms of PANO in a 0.10 M NaCl solution with pH 5.0, curves: (1) the first cycle, (2) the ninth cycle, (3) the tenth cycle, at a scan rate of 5 mV s^{-1} . (B) Cyclic voltammograms of PANO in a solution of 0.10 M NaCl containing various concentrations of dichromate at pH 5.0, curves: (1) without dichromate, (2) 1.0 mM, (3) 10 mM, and (4) 40 mM dichromate, at a scan rate of 5 mV s^{-1} .

40 mM dichromate is similar to that of curve 3, but the area of curve 4 is larger than that of curve 3. The area increment of cyclic voltammogram indicates the increase in the redox activity of PANOA, which clearly is caused by dichromate because of the equivalent pH for both solutions. As the concentration of dichromate increased, a new pair of redox peaks at lower potentials appears on curves 3 and 4. We are interested in a new reduction peak at -0.10 V on curve 4 in Fig. 1B. It is reasonable to suggest that this peak is caused by the reduction of dichromate at the PANOA-modified GCE because its peak current increases with increasing the concentration of dichromate. In addition, the net current of dichromate reduction, i.e. the current difference between curve 4 and curve 1 at -0.10 V in Fig. 1B is about $110 \mu\text{A}$, which is much larger than that between curve 2 and curve 1 in Fig. 1B at the same potential. This is strong evidence for the electrocatalytic reduction of dichromate caused by the PANOA copolymer. The PANOA copolymer can effectively catalyze dichromate reduction, which provides a new electrode material for the investigation of dichromate reduction and extends the application range of conducting polymers.

Typical UV–vis spectra of Cr(VI) after treatment at the PANOA-modified GCE is shown in Fig. 2A. To remove dichromate from the solution, PANOA films were first reduced at -0.30 V in a solution of 0.10 M NaCl with pH 5.0 for 30 min, and then were immediately moved into a 3 mL solution containing 0.10 M NaCl and 10 mM dichromate with pH 5.0 to be oxidized at 0.55 V for different intervals for a total doping period of 45 min. It can be seen clearly in Fig. 2A that there are two series of absorbance peaks. The band located at about 355 nm is characteristic of Cr(VI). As shown in Fig. 2A, the absorbance at 355 nm decreases with increasing doping time, which indicates that the Cr(VI) reduction occurs at the PANOA films.

Curves 1 and 2 in Fig. 2B show the FT-IR spectra of PANOA synthesized in the HCl solution and doped in 0.10 M NaCl solution containing 40.0 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ of pH 5.0, respectively. Table 1 presents the fundamental peaks of the PANOA films. The peak at about 3430 cm^{-1} is attributed to the N–H stretching vibrations. The peaks observed at about 1570 and 1480 cm^{-1} are attributed to the C=C stretching vibrations of quinine ring and benzene ring vibrations, respectively. The peak at about 1385 cm^{-1} can be assigned to C–O–H deformation vibrations. The peaks at about 1330 , 1220 , 800 cm^{-1} are attributed to the C–O stretching vibrations, C–N stretching vibrations and C–H out-of-plane bending vibration, respectively. According to the literature [29], the appearance of two new peaks at 1624 and 949 cm^{-1} in curve 2 (Fig. 2B) is like to correspond to Cr–O vibrations, which is strong evidence for that the Cr was incorporated in PANOA films during the doping process.

3.3. Schematic model for the electrochemical reduction of Cr(VI)

To further understand the electrocatalytic reduction and removal process, ESR technique was used to approach the effect of $\text{Cr}_2\text{O}_7^{2-}$ doped into the PANOA on the ESR signal. Curves 1 and 2 in Fig. 3 show the spectra of emeraldine salt of PANOA synthesized in HCl solution and doped PANOA obtained in a solution containing 0.10 M NaCl and

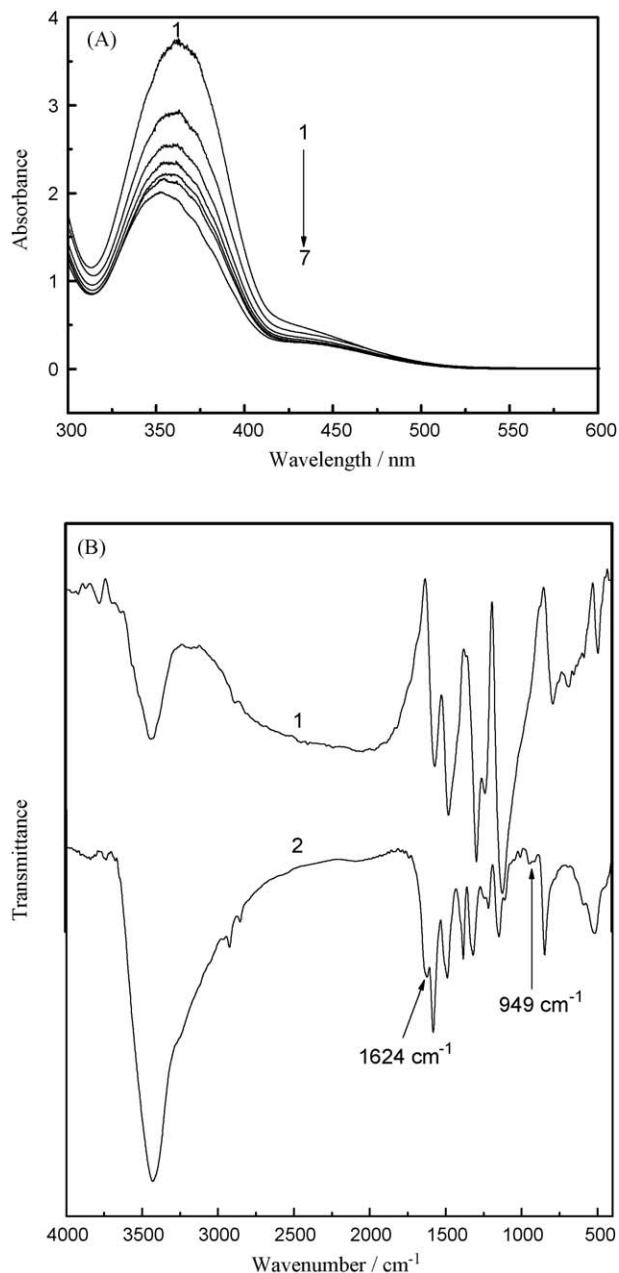


Fig. 2. (A) UV–vis spectra of a 0.10 M NaCl + 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ solution (pH 5.0) as a function of time during treatment with PANOA-modified GCE. Curves: (1) 0 min, (2) 2 min, (3) 5 min, (4) 10 min, (5) 20 min, (6) 30 min, (7) 45 min. (B) FT-IR spectra of PANOA films. Curves: (1) as-prepared PANOA at the oxidized state, (2) PANOA doped in the solution consisting of 0.10 M NaCl and 40 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ with pH 5.0.

40 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ of pH 5.0, respectively. Both sample used here are at the same oxidation state. The microwave power for curves 1 and 2 is 2.00 and 20.07 mW, respectively. It is interesting to point out that curve 2 has two ESR signals. The g-factor of PANOA is 2.00287 . While

Table 1

The fundamental peaks of the PANOA films.

Sample	N–H stretching vibration (cm^{-1})	C=C stretching vibration (cm^{-1})		C–O–H deformation vibration (cm^{-1})	C–O stretching vibration (cm^{-1})	C–N stretching vibration (cm^{-1})	C–H out-of-plane bending vibration (cm^{-1})
		Benzene ring	Quinine ring				
1	3436	1583	1445	1386	1294	1230	787
2	3430	1569	1478	1384	1320	1218	849

Sample 1: PANOA synthesized in 2.0 M HCl; sample 2: doped PANOA obtained in a solution containing 0.10 M NaCl and 40 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ of pH 5.0.

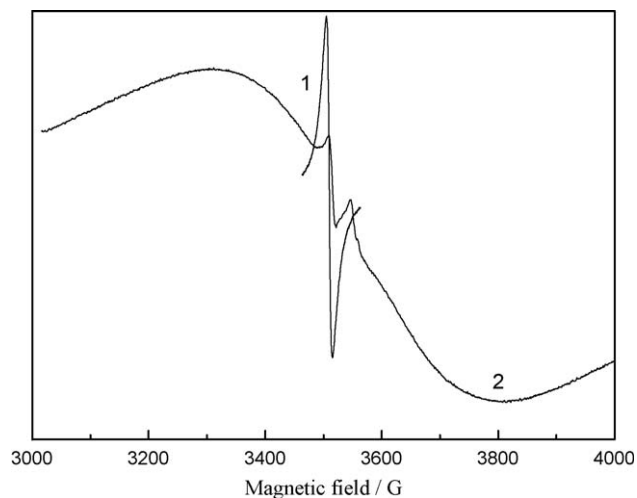
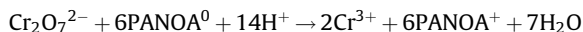


Fig. 3. ESR spectra of PANO films. Curves: (1) as-prepared PANO at the oxidized state, (2) PANO doped in the solution consisting of 0.10 M NaCl and 40 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ with pH 5.0.

the doped PANO has two *g*-factors, 2.00274 and 1.98171, respectively. The signal at about 3500 G is attributed to the PANO itself. The broad peaks can be attributed to the Cr(III) in PANO films according to the literature [30].

As expected, the ESR spectra presented here give strong evidence that the Cr(VI) can be removed and reduced to less-toxic Cr(III). The reduction of Cr(VI) at PANO films describes as follows:



To confirm the presence of Cr and study the surface composition of PANO, XPS was used to characterize PANO samples. Fig. 4A shows the XPS spectra of the PANO synthesized in the HCl solution at the oxidation state (curve 1), doped PANO obtained in a solution containing 0.10 M NaCl and 40 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ of pH 5.0 (curve 2) and dedoped PANO (curve 3). As shown in Fig. 4A, all the PANO films are composed of C, N and O. The peaks at about 200 eV in curves 1 and 3 are attributed to Cl. It is worth noting that no peak appears at about 200 eV in curve 2, while two additional peaks appear at 577 and 587 eV (Fig. 4B). These two peaks are correspond to $\text{Cr}_{2p_{3/2}}$ and $\text{Cr}_{2p_{1/2}}$, which indicates that the Cr(VI) can be successfully doped in PANO and electrochemically reduced to Cr(III).

Table 2 shows the surface composition of PANO films at different states. On the basis of the data listed in Table 2, 3.47% Cl is contained in the sample 1 that was synthesized in 2.0 M HCl. Its doping level Cl/N is 29.4%. Sample 2, obtained by the oxidation of PANO in the solution consisting of 0.10 M NaCl and 40.0 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, contains 6.31% Cr and 0.42% Cl. Its doping level is 78.2%. It is worth noting that the doping level of sample 2 is much higher than that of sample 1, which indicates that the doping process is effective. Furthermore, only a trace amount of Cl (0.42%) was detected in sample 2, which means that the PANO has very good ion selectivity in the 0.10 M NaCl supporting electrolyte. This is because the higher

Table 2

Surface composition (in at.%) of PANO films at different states.

Sample	C _{1s}	O _{1s}	N _{1s}	Cr _{2p}	Cl _{2p}	Doping level
1	79.90	4.82	11.81	0.00	3.47	29.40
2	62.02	22.65	8.61	6.31	0.42	78.17
3	74.01	12.28	9.66	1.92	2.13	41.92

Sample 1: PANO synthesized in 2.0 M HCl; sample 2: doped PANO obtained in a solution containing 0.10 M NaCl and 40 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ of pH 5.0; sample 3: dedoped PANO.

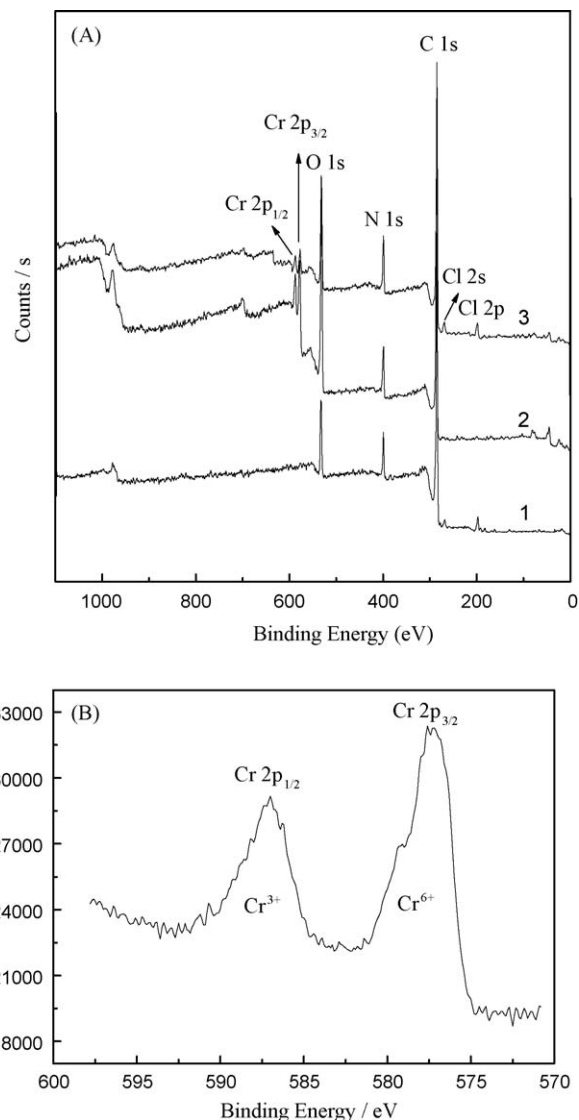


Fig. 4. (A) XPS spectra of PANO films. Curves: (1) as-prepared PANO at the oxidized state, (2) PANO doped in the solution consisting of 0.10 M NaCl and 40 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, (3) dedoped PANO. (B) XPS spectra of high resolution scan of Cr of curve 2 (A).

negative charge favors uptake of the dichromate. It can be seen in sample 3 that a large amount of Cr is removed during the dedoping process, which suggests that the Cr(VI) removal process at the PANO-modified GCE is recyclable. However, a small amount of Cr and Cl remained in the reduced PANO. This is due to the fact that the reduction potential was not negative enough and therefore the reduction of PANO cannot be completely performed in the 0.10 M NaCl solution.

According to the results of ESR spectra and XPS, we present the reduction and doping mechanism of dichromate (Fig. 5). Step 1: the PANO film (oxidation state or PANO^+A^-) was synthesized at 0.79 V on a GCE, where A^- represents to Cl^- . Step 2: the well-washed PANO-modified GCE was immersed in 0.10 M NaCl solution with pH 5.0. At the negative potentials, the emeraldine salt of PANO (oxidation state or PANO^+A^-) is quickly reduced to leucoemeraldine (reduction state or PANO^0). Step 3: the prepared PANO-modified GCE was immersed in a dichromate solution. When a anode potential is applied, the reduction state PANO converts to oxidation state with the Cr(VI) doping into the PANO films (Reaction (2), Fig. 5) and part of the Cr(VI) reduces to Cr(III) (Reaction (1), Fig. 5). Step 4: when a cathodic potential is applied

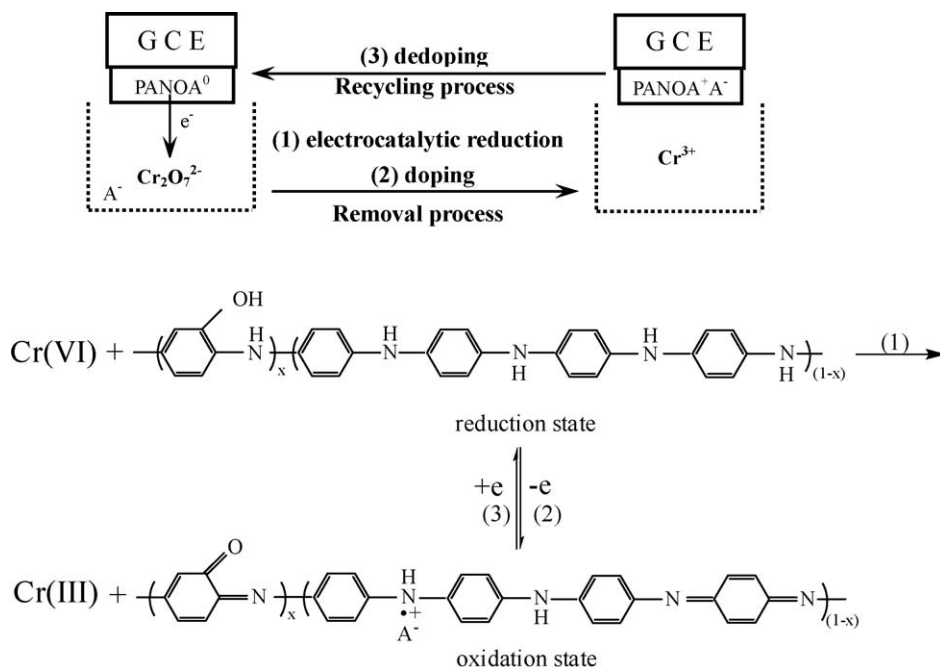


Fig. 5. Schematic model for the electrochemical reduction and removal of Cr(VI) using PANO in a wide range of pHs.

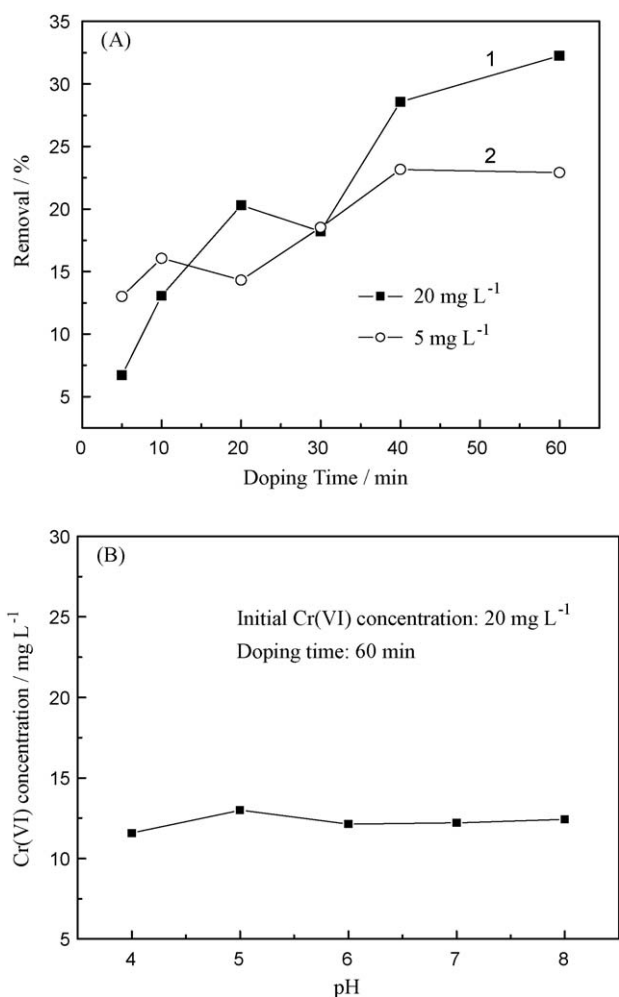


Fig. 6. (A) Effect of initial Cr concentration on the reduction, curves: (1) 20 mg L⁻¹, (2) 5 mg L⁻¹. (B) Effect of pH on the reduction of Cr. The PANO film was grown to 4 C polymerization charge on a 1 cm² Pt working electrode, initial Cr(VI) = 20 mg L⁻¹, doping time = 60 min.

again, the PANO matrix returns to its reduced state with no or negative charge, causing the doped anions to be released (i.e. dedoping) (Reaction (3), Fig. 5).

3.4. Effect of initial Cr(VI) concentration and pH on the Cr(VI) reduction

The following results based on a 1 cm² Pt working electrode, which had relative larger surface area. The PANO film, which was grown to 4 C polymerization charge at 0.77 V, had similar electrochemical activity, stability and reversibility to the PANO films synthesized on the GCE. The prepared PANO-modified Pt electrode was then transferred to a 200 mL dichromate solution with different initial concentrations or pHs. At every given doping time, 4 mL dichromate solution was collected and measured by flame atomic absorption spectroscopy. Fig. 6A shows the plot of removal rates of various initial concentrations of Cr(VI) (solution pHs 5.0) versus doping time. From Fig. 6A, two important conclusions can be drawn. First, the removal rates of both curves increase with the increasing of doping time. Second, various initial concentrations of the Cr(VI) have different removal rates. When the doping time is less than 10 min, the removal rate of curve 2 is better than that of curve 1. However, curve 1 has the better removal rate, when the doping time is more than 13 min. The maximum removal rate of Cr(VI) was found to be 32.3% when the doping time was 60 min and the initial Cr(VI) concentration was 20 mg L⁻¹. Fig. 6B shows the effect of pH on reduction of Cr. The doping processes were carried out in a wide range of pHs, from pH 4 to pH 8. As shown in Fig. 6B the PANO films have similar removal rate, which means the PANO films have excellent electrochemical activity and stability in a wide range of pHs. This result is in good agreement of the literature [26]. Therefore, the PANO can be a promising material for the reduction of Cr(VI) in the solution pH range of 4–8.

4. Conclusion

The current work demonstrates that the PANO can be successfully used to remove dichromate and is effective for partial

reduction of Cr(VI) to less-toxic Cr(III) in the pH range of 4–8. The good electrochemical stability and redox properties in a wide range of pHs make PANOA a new electrode material for the investigation of dichromate reduction. Based on the result of XPS and doping–dedoping principle of PANOA, a large amount of the doped dichromate is removed in the dedoping process, which suggests that the Cr(VI) removal process at the PANOA-modified GCE is recyclable. However, further study is needed to improve the effectiveness of the reduction. It is expected that the electrically switched anion exchange would be a green process and an attractive route to remove Cr(VI) in wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apcatb.2009.08.014](https://doi.org/10.1016/j.apcatb.2009.08.014).

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